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**ENRICHMENT OF OXYGEN FOR THE PRODUCTION OF HYDROGEN FROM
HYDROCARBONS WITH CO₂ CAPTURE**

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The present invention concerns a method and a device for producing hydrogen from a hydrocarbon with high energy efficiency while releasing low or zero levels of carbon dioxide and pollutants.

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In the sense of the present invention, the term hydrocarbon generally designates any fossil or renewable fuel, including substances that are oxygenated (alcohol, ester, etc.), gaseous, liquid, or even in powdered solid form (handleable like a fluid), provided that it forms only a small amount of inert solid residue, i.e., an ash content of less than 1% by weight.

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In essence, hydrogen as such does not exist in a natural state and must be produced, for example for use in fuel cells, either in a centralized way in order to be distributed to local retailers and users, or in a decentralized way, locally, just upstream from the fuel cell, for immediate consumption by the latter.

Hydrogen can be produced from two separate sources: either by so-called
30 "downstream" means, i.e. by breaking down water thermally at a very high

REPLACEMENT PAGE (RULE 26)

temperature or electrically by electrolysis, or by so-called “upstream” means, by converting a hydrocarbon.

Since the hydrogen is intended to subsequently produce electricity in a fuel cell, the use of “electrolysis” may seem inappropriate, at least in terms of overall energy efficiency.

5 But if this electricity is from a renewable (wind, solar, geothermal) or nuclear source, there is no production of CO₂ or other pollutants in this production-consumption chain. Whether for stationary or mobile applications, the hydrogen in that case seems to be an energy vector, making it possible, through the use of fuel cells, to produce clean electricity in places that are totally or periodically without access to nuclear or renewable energy.

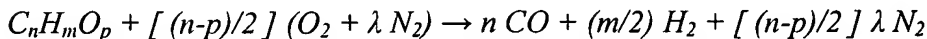
10 In the “upstream” method, the conversion of a fossil or renewable hydrocarbon generates hydrogen but also CO₂, which may limit the advantage of using fuel cells. However, this method has the advantage of potentially high energy efficiency, thus conserving fossil fuel resources or biomass products for energy uses.

There is therefore an emerging need for technologies for the centralized (large-scale) or decentralized (small-scale) production of hydrogen with high energy efficiency and low generation of CO₂ or other pollutants.

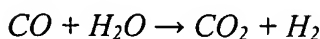
There are three main families of known methods for producing a hydrogen-rich mixture. These three methods are described theoretically below:

1. First family: Partial Oxidation combined with Water-Gas Shift Conversion (POX + WGS).

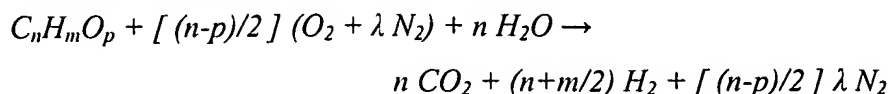
The partial oxygen (POX) reaction corresponds to the reaction of the fuel (C_nH_mO_p) with oxygen. It results in the formation of gaseous mixture of hydrogen, carbon monoxide, and possibly nitrogen (if the oxygen is drawn from the air):



25 λ represents the N₂/O₂ molar ratio of the oxidant mixture (standard air or oxygen-enriched air: $\lambda < 3.762$). The POX reaction is exothermic; it does not require an external supply of heat. Having extracted the hydrogen from the fuel, it is possible to produce more of it using the so-called water-gas shift or WGS reaction, in which the carbon monoxide reacts with the water vapor to form carbon dioxide and additional hydrogen through the following reaction:



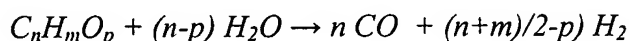
Finally, the combination of the POX and WGS reactions is written as follows:



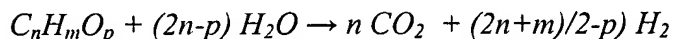
POX, being endothermic, produces less hydrogen than the vapor reforming (second family of methods) described below, and moreover, has a tendency to produce solid carbon, which can foul or clog the tubes and exchangers. For example, in the case of gasoline, it is performed at around 1200°C without a catalyst and at around 800°C with a catalyst. For diesel fuel, it is conducted between 950°C and 1200°C (Texaco-Shell™ burners).

2. Second family: Complete Vapor Reforming (VRC)

It is also possible to produce hydrogen from the fuel using the vapor reforming (VR) reaction, the principle of which is to oxidize the carbon in the fuel by reducing the number of water molecules in the gaseous phase.



This reaction, automatically performed on a catalyst, is very highly endothermic: this means that it requires an external supply of heat, which makes the generating system complex. This supply may be produced either through external combustion of a fraction of fuel, or by recovering excess heat. The concatenation of the VR and WGS reactions is known as Complete Vapor Reforming (VRC) of the fuel, and is written as follows:



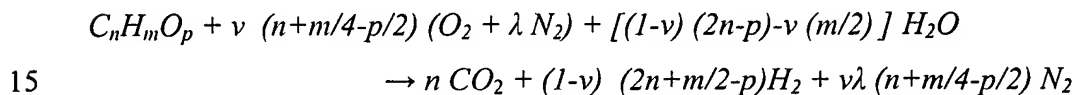
Vapor reforming is a reaction that is well known in petrochemistry, where the production of hydrogen from natural gas is common. It requires a nickel-based catalyst, adapted to the molecules to be reformed (methane and light hydrocarbons). It is done at a temperature of 850 to 950°C at pressures of 15 to 25 bar and at H₂O/F (fuel) ratios between 2 and 4. These reactions, being endothermic, are conducted in large furnaces or banks of parallel tubes filled with catalysts and heated externally (mainly by radiation), which are passed through by the mixture to be reformed. The energy required for the reforming reaction is produced by oxidizing part of the fuel with air (producing CO₂ and H₂O) and is transmitted to the reagents to be reformed through the walls of these tubes.

For other hydrocarbons, the conditions and catalysts are different. For hydrocarbons that are heavier than methane, the temperatures are lower than for methane (850°C). Methanol is easier to reform; temperatures of 250°C are sufficient, and the catalyst is

Cu/Zn/Al-based. Reforming gasoline requires a temperature higher than 800°C. Hydrocarbons that contain sulfur require pre-desulphurization, as the catalyst would be poisoned by the sulfur. The reforming is therefore done under temperature and pressure conditions that are adapted to the fuel and that can be calculated using the laws of thermodynamics involving chemical equilibrium. It is always a slow reaction, which is why the reforming is necessarily catalytic.

3. Third family: Autothermal Vapor Reforming (VRA)

In this method, a fraction of the fuel, which we'll call v , is burned in the reformer in order to supply exactly enough energy to produce the endothermic complete vapor reforming reaction of the remaining fraction $(1-v)$ of the fuel. The Autothermal Vapor Reforming reaction is thus theoretically athermal. It is usually produced catalytically, at temperature levels between that of the POX-based method and that of the VRC method, for example on nickel at 25 bar and at 950°C. It is written in the following way:



The fraction v that should be burned depends solely on the atomic composition of the fuel and its heat-generating power, as well as that of the hydrogen. VRA is a combination of reforming and partial oxidation (with water and air injection). This technology has been adapted for small-scale facilities both in EPYX™ technology and in single-reactor HOTSPOT™ technology, initially developed for methanol.

In all reforming techniques, there is an energy need that is satisfied by oxidizing part of the fuel with atmospheric air. This oxidation takes place outside the hydrogen producing reactor in the case of vapor reforming, or inside the hydrogen producing reactor in the case of partial oxidation and autothermal vapor reforming. It consumes oxygen and produces CO₂.

The air is compressed before being introduced into the reforming process. In the case of a reforming process in connection with a fuel cell, air is also compressed in order to be introduced into the fuel cell. The air compressors represent auxiliary equipment that consumes a significant part of the electric power produced by the fuel cell. To limit this consumption, the tendency is to use low levels of pressurization relative to the atmospheric pressure, both for the fuel cell and for the reforming process when it is performed in direct connection with a fuel cell.

The invention concerns a method for producing hydrogen from a hydrocarbon with high energy efficiency while releasing very low or zero levels of carbon dioxide and pollutants.

The method comprises a step (a) for using a flow of (pure or nearly pure) oxygen to
5 (i) oxidize a portion of the hydrocarbons and (ii) supply the heat required to convert, using water vapor, at suitable temperatures, nearly all of the other portion of the hydrocarbons into hydrogen, carbon monoxide and carbon dioxide. Suitable temperatures means temperatures like those used in the techniques described above.

The method also comprises a step (b) for preheating the hydrocarbons, the flow of
10 oxygen and the water to be vaporized. The hydrocarbons, the flow of oxygen, and the water to be vaporized are hereinafter referred to as the reagents.

The result of this combination of technical characteristics is that, nitrogen being absent from the reagents, there is no generation of nitrous oxide and no need for energy to preheat it. The hydrogen production yield is thus distinctly improved.

15 The mixture formed by the hydrogen, the carbon monoxide, the carbon dioxide and the excess water vapor is hereinafter referred to as the products of the conversion. Nitrogen being absent from the reagents, it does not dilute the conversion products; the subsequent steps (b) through (f) of the method are facilitated, and overall efficiency is increased.

The method also comprises steps (c) for cooling (at least one) of the conversion
20 products in order to recover a fraction of the thermal energy of the conversion products for the purpose of preheating the reagents and condensing at least part of the water vapor contained in the conversion products.

The method also comprises the following steps:

- a step (d) for recovering the hydrogen by extracting the hydrogen from the
25 conversion products, either in order to consume it or with a view to storing it for later consumption.

Steps (a) through (d) are performed at suitably high pressures, above 30 bar, in order to:

- intensify the heat exchanges, and/or
- 30 • increase the compactness of the method, and/or
- promote the liquefaction of the carbon dioxide by cooling, and/or

- promote the condensation of the water vapor by cooling, and/or
- improve the overall efficiency.

Preferably, the method according to the invention also comprises:

- steps (e) for the final conversion of the carbon monoxide into carbon dioxide; if
5 necessary, these steps are performed during the step for recovering the hydrogen.

The result of this combination of technical characteristics is that, at the end of steps (a) through (e), the residual flow no longer contains, apart from the water vapor that has not yet condensed, anything other than carbon dioxide.

10 Preferably, the method according to the invention is performed at sufficient pressure to implement:

- a step for condensing (f) the carbon dioxide contained in the conversion products and/or the final conversion products,
- a step for capturing the carbon dioxide in liquid form.

15 Preferably, the method according to the invention uses a membrane that is selectively permeable to hydrogen to extract the hydrogen from the conversion products. In the case of this variant of embodiment, the method also comprises a step for lowering the partial pressure of the hydrogen downstream from the membrane by diluting the flow of permeated hydrogen in a flow of extraction gas, particularly a condensable gas. The result of this combination of technical characteristics is that the permeation of the hydrogen is facilitated.

20 Preferably, in the case of this variant of embodiment of the invention, the extraction of hydrogen by means of a permeable membrane is performed at the same time as the step for the final conversion of the carbon monoxide into carbon dioxide. The result of this combination of technical characteristics is that the partial pressure of the hydrogen during the final conversion step is lowered, which promotes the conversion of the carbon monoxide into
25 carbon dioxide.

Preferably, in the case of this variant of embodiment of the invention, the method also comprises a step for regulating the temperature of the final conversion by adjusting the flow rate and/or the temperature of the flow of extraction gas.

30 Preferably, according to the invention, the method is such that the preheating and cooling steps are combined in a recovery exchanger so that the reagents and the conversion products circulate continuously through the recovery exchanger.

Preferably, in the case where the method is more specifically intended to produce hydrogen for the purpose of feeding a fuel cell running with air, the method according to the invention also comprises a step for lowering the pressure of the conversion products and/or the final conversion products and/or the hydrogen produced while compressing the air required to run the fuel cell.

Preferably, the method according to the invention can also be combined with a hydrogen production method that generates a flow of oxygen, particularly by electrolysis. The result of this combination of technical characteristics is that it is thus possible:

- to limit the cost of producing the oxygen consumed in the method according to the invention, and
- to increase the overall quantity of hydrogen produced.

Preferably, the method according to the invention can also be combined with a nitrogen production method that generates a flow of oxygen. The result of this combination of technical characteristics is that it is thus possible to limit the cost of producing the oxygen consumed in the method according to the invention.

The invention concerns a device for producing hydrogen from a hydrocarbon with high energy efficiency while releasing very low or zero levels of carbon dioxide and pollutants. The device comprises a reactor for converting (a) the hydrocarbons using water vapor. The conversion reactor is supplied with pure or nearly pure oxygen in order to (i) oxidize a portion of the hydrocarbons and (ii) supply the heat required to convert into hydrogen, carbon monoxide and carbon dioxide, at suitable temperatures, nearly all of the other portion of the hydrocarbons. The mixture formed by the hydrogen, the carbon monoxide, the carbon dioxide and the excess water vapor is hereinafter referred to as the products of the conversion.

The device also comprises means for preheating (b) the hydrocarbons, the flow of oxygen and the water to be vaporized. The hydrocarbons, the flow of oxygen and the water to be vaporized are hereinafter referred to as the reagents.

The device also comprises:

- at least one heat exchanger (c) for (i) cooling the conversion products, for (ii) recovering a fraction of the thermal energy from the conversion products in order to preheat

the reagents, and for (iii) condensing at least a part of the water vapor contained in the conversion products.

- a hydrogen recovery unit (d).

5 The hydrogen recovery unit comprises an extraction element for extracting the hydrogen from the conversion products in order to consume it in a hydrogen-consuming device (for example in a fuel cell) or store it in a reservoir for later consumption.

The conversion reactor, the preheating means, the heat exchanger, and the recovery unit operate at suitably high pressures, above 30 bar, in order to:

- intensify the heat exchanges, and/or
- 10 • increase the compactness of the method, and/or
- promote the liquefaction of the carbon dioxide by cooling, and/or
- promote the condensation of the water vapor by cooling, and/or
- improve the overall efficiency.

Preferably, the device according to the invention also comprises:

- 15 - at least one reactor for the final conversion (e) of the carbon monoxide into carbon dioxide, if necessary combined with the hydrogen recovery unit.

The result of this combination of technical characteristics is that the residual flow that leaves the device according to the invention no longer contains, apart from the water vapor not yet condensed, anything other than carbon dioxide.

20 Preferably, according to the invention, the pressure inside the device is sufficient to implement:

- a condenser (f) for condensing the carbon dioxide contained in the conversion products and/or the final conversion products,

- a container for storing the carbon dioxide in liquid form.

25 Preferably, according to the invention, the extraction element includes a membrane that is selectively permeable to hydrogen for extracting the hydrogen from the conversion products. The extraction element also includes a feed of extraction gas, particularly an easily condensable gas, located downstream from the membrane, which lowers the partial pressure of the hydrogen downstream from the membrane by diluting the flow of permeated hydrogen. The result of this combination of technical characteristics is that the permeation of
30 the hydrogen is facilitated.

Preferably, in the case of this variant of embodiment of the invention, the extraction element with a permeable membrane is disposed in the final conversion reactor. The result of this combination of technical characteristics is that the partial pressure of the hydrogen during the final conversion is lowered, which promotes the conversion of the carbon
5 monoxide into carbon dioxide.

Preferably, in the case of this variant of embodiment of the invention, the device also comprises means for regulating the temperature of the final conversion by acting on the flow rate and/or the input temperature of the extraction gas.

Preferably, in the case of this variant of embodiment of the invention, the device is
10 such that the permeable membrane is composed of a plurality of tubes that descend into the extraction element. Each tube is shaped like a glove finger whose open end opens to the outside of the extraction element. The open end makes it possible to introduce the extraction gas into the tube.

Preferably, the device according to the invention is such that the preheating means
15 and the cooling heat exchanger are combined in a recovery exchanger so that the reagents and the conversion products circulate continuously through the recovery exchanger.

Preferably, in the case where the device is more specifically intended to produce hydrogen for the purpose of supplying a fuel cell running with air, the device according to the invention also comprises an element for reducing the pressure of the conversion products
20 and/or the final conversion products and/or the hydrogen produced, making it possible to compress the air required to run the fuel cell.

Preferably, the device according to the invention can also be combined with a hydrogen production unit that generates a flow of oxygen, particularly by means of an electrolyzer. The result of this combination of technical characteristics is that it is thus
25 possible:

- to limit the cost of producing the oxygen consumed in the method according to the invention, and
- to increase the overall quantity of hydrogen produced.

Preferably, the device according to the invention can also be combined with a
30 nitrogen production unit that generates a flow of oxygen. The result of this combination of

technical characteristics is that it is thus possible to limit the cost of producing the oxygen consumed in the method according to the invention.

Other characteristics and advantages of the invention will become apparent through the reading of the description of variants of embodiment of the invention given as an illustrative and non-limiting example, and of

- Fig. 1, which illustrates the variation in the fraction (f_a) of hydrocarbon oxidized with pure oxygen as a function of the reagent preheating temperature in the case of diesel fuel,

- Fig. 2, which illustrates the variation in the fraction (f_a) of hydrocarbon oxidized with air as a function of the reagent preheating temperature in the case of diesel fuel,

- Fig. 3, which illustrates, in block diagram form, a variant of embodiment of a unit for producing pure hydrogen stored under pressure,

- Fig. 4, which illustrates, in block diagram form, another variant of embodiment of a unit for producing pure hydrogen, intended to be used immediately in a low-temperature, low-pressure PEMFC-type fuel cell,

- Fig. 5, which illustrates, in block diagram form, another variant of embodiment of a unit for producing a mixture of hydrogen and carbon dioxide, intended to be used immediately in a low-temperature, medium-pressure PEMFC-type fuel cell,

- Fig. 6, which illustrates in block diagram form, another variant of embodiment of a unit for producing a mixture of hydrogen and carbon dioxide, intended to be used immediately in a high-temperature, medium-pressure SOFC-type fuel cell,

- Fig. 7, which illustrates a variant of embodiment of a means for preheating the reagents and a heat exchanger for cooling the associated products, constituting a regeneration system, the regeneration system being combined with a conversion reactor,

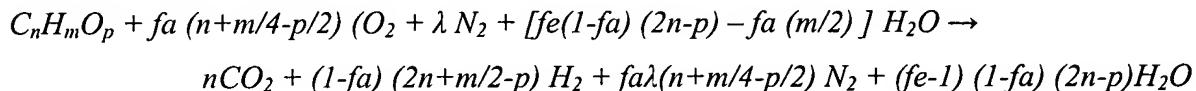
- Fig. 8, which illustrates another variant of embodiment of a means for preheating the reagents and a heat exchanger for cooling the associated products, constituting a recovery exchanger, the recovery exchanger being combined with a conversion reactor,

- Fig. 9, which illustrates in a graph the increase in the efficiency of the hydrogen permeation as a function of the ratio between the molar flow rate of the extraction gas downstream from the membrane and the molar flow rate of the hydrogen to be extracted upstream from the membrane,

- Figs. 10a and 10b, which illustrate a reactor for converting CO into CO₂ equipped with a hydrogen-permeable membrane, supplied with extraction water vapor on the downstream end

- Fig. 11, which illustrates a reactor for converting CO into CO₂, equipped with a series of closed-end tubes that descend into the core of the reactor, each of which supports a hydrogen-permeable membrane.

We will now describe Fig. 1. This figure illustrates the variation in the fraction (fa) of hydrocarbon oxidized with pure oxygen as a function of the reagent preheating temperature in the case of diesel fuel. As this graph shows, and as the description below explains, the fraction (fa) of hydrocarbon oxidized depends on the desired conversion temperature. The curves shown respectively correspond to the following conversion temperatures (Tconv): 1000°C, 1200°C, 1400°C. They have been plotted for water factor (fe) values equal to 1.5 and a pressure of 5 bar. In the sense of the present invention, the term water factor (fe) means the ratio between the flow of water actually made available by injection into the conversion reactor and the stoichiometric flow of water required for a complete conversion of the fraction of hydrocarbon to be converted:



The water factor has an influence on the formation of soot, carbon particles or polyaromatic hydrocarbons during the conversion. Fig. 1 shows that fa diminishes when the preheating temperature of the reagents increases. In fact, the amount of energy supplied with preheated reagents makes it possible to reduce the fraction of fuel to be burned in order to reach the desired temperature level and to promote the endothermic conversion reactions.

Such figures can be established for each fuel or mixture of fuels and are not specific to diesel fuel. Nor are they specific to the reforming method used (vapor reforming or partial oxidation, catalytic or non-catalytic, etc.).

Any conversion of a hydrocarbon into hydrogen using water vapor, possibly in the presence of oxygen, requires obtaining a sufficient temperature level in the conversion reactor. The temperature level to be applied depends both on the hydrocarbon to be converted and on whether or not a catalyst is present. For example, in the case of a catalytic vapor reforming type reaction, a temperature of 200 to 250°C is sufficient in the case of methanol.

If on the other hand the fuel is methane, temperatures of 800 to 950° are necessary. The partial oxidation of gasoline can be conducted at 800°C in the presence of a catalyst and at 1200°C in the absence of a catalyst. Non-catalytic conversion using water vapor requires 1200°C for any fuel and 1400°C to obtain in less than one second a complete conversion, i.e., one that releases products that are free of even light hydrocarbons such as methane, ethane or ethylene.

It order to reach these temperature levels at the end of conversion, it is wise to preheat the reagents. A portion of this preheating heat can be recovered by cooling the products that leave the conversion reactor, and transferred to the reagents through external exchange. On the other hand, it is technologically easier, and also faster, to supply heat to gasses at a high temperature (higher than 800°C, for example) by oxidizing a fraction of the fuel, either with air, with oxygen, or with an oxygen-rich flow; the other, non-oxidized fraction of this fuel being converted into a mixture of hydrogen and carbon monoxide and dioxide.

For an adequate conversion temperature, a given water factor and a chosen reagent preheating temperature, the fraction f_a and the flow of oxygen can be determined, as shown in Fig. 1. Thus, the three reagent flows to be placed in contact inside the conversion reactor are identified.

The introduction into the conversion reactor of the preheated reagents, and in particular pure oxygen, generates highly active oxidation zones in contact with the hydrocarbon, which can lead to very high temperatures, for example higher than 2500°C. In the present invention, one must therefore be careful:

- (i) first, to simultaneously introduce the hydrocarbon and the water vapor required for the conversion, so that the water vapor absorbs part of the energy given off by the oxidation of the hydrocarbon,
- (ii) second, to organize the gradual injection of the reagents into the reactor and their mixture inside this reactor so as to gradually release the oxidation energy, as well as the energy required for the conversion, and thus establish a satisfactory temperature profile inside the reactor, and
- (iii) and possibly, to provide thermal protection for the walls, for example using a parietal film of hydrocarbons and/or water vapor that is relatively cool compared to the reaction mixture.

The combination of these technical characteristics, and in particular the proper use of a flow of nearly pure oxygen, makes it possible to obtain a nearly complete conversion of the hydrocarbon into hydrogen and CO/CO₂: light hydrocarbons such as methane, ethylene, and ethane, as well as polyaromatic hydrocarbons, are present only in trace amounts. Thus, the products of the conversion contain only H₂, CO, CO₂ and H₂O and are not diluted in nitrogen.

The hydrogen conversion reaction being endothermic, no matter how high the preheating temperature, it will be necessary in all cases to oxidize a fraction of the hydrocarbon in order to compensate for the heat of the conversion reaction. This minimum fraction to be burned can be determined as a function of the fuel's enthalpy of formation and its composition. This particular value of f_a is marked v . This value is characteristic of the fuel. It is equal to 0.2565 in the case of diesel fuel.

Knowing the value of f_a and the value of v relative to the fuel makes it possible to directly determine the value of the hydrogen production yield, give or take a few losses, in the subsequent steps of the method. The yield η is equal to:

$$\eta = (1 - f_a) / (1 - v)$$

In the case of a non-catalytic conversion of diesel fuel with oxygen at 1400°C, with a preheating of the reagents at 700°C, the yield is equal to:

$$\eta = (1 - 0.374) / (1 - 0.2656) = 0.852.$$

The flows of oxygen and diesel fuel to be used are therefore in a ratio of 1.27. A higher preheating temperature, with exchangers made of ceramic material, produces better yields. Yields of 80 to 90% are therefore attainable with the technology according to the invention for oxygen and diesel fuel consumption in a ratio of 1.15 to 1.40 and hydrogen production yields of 0.283 to 0.253 kg H₂ per kg of diesel fuel.

If air were used instead of oxygen, the value of v would be unchanged, but higher values of f_a would be required to reach the same conversion temperatures. In fact, it is necessary to heat all of the nitrogen that is injected into the conversion reactor at the same time as the oxygen. Fig. 2 illustrates, in the case of diesel fuel, the variation in the fraction (f_a) of hydrocarbon oxidized with air as a function of the reagent preheating temperature. To facilitate the comparison of Figs. 1 and 2, the desired conversion temperatures are the same (1000, 1200 or 1400°C) as are the water factor $f_e = 1.5$ and the pressure $P = 5$ bar.

Thus, for diesel fuel, for a conversion temperature equal to 1400°C and a preheating at 700°C, a value of f_a equal to 0.444 is necessary. From this, it may be deduced that the conversion yield with air is:

$$\eta = (1-f_a) / (1-v) ; \text{ or } \eta = (1-0.444) / (1-0.2656) = 0.757$$

5 This yield is clearly more advantageous than with pure oxygen (0.852).

Moreover, with air, the oxidation of the fraction of the fuel and the conversion of the remaining fraction are less sudden than with oxygen. The maximum temperatures reached are lower, and there may remain larger contents of light hydrocarbons such as methane, ethylene and ethane as well as polyaromatic hydrocarbons. These contents are on the order of
10 a few per thousand to a few percent, depending on the family of conversion methods used and the temperature applied.

We will now demonstrate that the use of pure or nearly pure oxygen makes it possible to operate under pressure, which has several advantages. We will also demonstrate that it is possible to use pure or nearly pure oxygen under pressure without thereby reducing the yield.

15 Reforming units on petrochemical sites commonly operate at high pressures of several tens of bar. On the other hand, for a small-scale unit that feeds, for example, a low-pressure fuel cell, using a partial oxidation or autothermal vapor reforming unit at high pressure is detrimental to the overall efficiency of the system since it is necessary to compress the air to be injected into the conversion reactor, which is energy-expensive. It is
20 therefore preferable to operate at a pressure close to the atmospheric pressure.

Conversely, in the case of the present invention, with a supply of oxygen rather than air, the cost of compressing the oxidant becomes negligible : either the oxygen is supplied in gaseous form in bottles or reservoirs already compressed to 200 bar or more, or the oxygen is supplied in liquid form under a few bar of pressure, but the compression energy of the liquid
25 is negligible. It is therefore possible and advantageous to perform the hydrogen production steps between 30 and 60 bar; this technical characteristic provides several advantages:

(i) The high pressures of the gasses lead to higher gas densities, higher heat exchange coefficients through the walls, and often also faster chemical kinetics, making it possible to considerably reduce the size of the equipment of the method.

30 (ii) The high pressure of the products makes it possible to use a hydrogen-permeable membrane, a membrane that normally requires typical partial pressure difference of 15 bar

(in reality from a few bar to 40 or 50 bar), in order to efficiently extract hydrogen and separate CO₂ and H₂, as explained below.

(iii) The high pressure of the products makes it possible, after cooling, to easily condense the water contained in the products and to recycle it for use in the conversion
5 reactor.

(iv) The high pressure of the products makes it possible in certain cases, as explained below, to condense the carbon dioxide.

(v) With a method of production between 30 and 60 bar, the pressure of the products can also be skillfully used, as explained below, to reduce the use of energy-expensive
10 auxiliary equipment and thus increase the overall efficiency of the installation.

A hydrogen production unit according to the invention can be embodied in various ways. Four variants of embodiment are shown as examples in Figs. 3 through 6.

We will now describe Fig. 3, which illustrates, in block diagram form, a variant of embodiment of a unit for producing pure hydrogen stored under pressure.

15 The production unit, also called the device 1, is composed of the following elements:

- a hydrocarbon reservoir: 2
- a reservoir for oxygen under pressure or in liquid form: 3
- a CO + H₂ conversion reactor at 60 bar: 4
- a means for preheating the reagents: 5
- 20 - a first heat exchanger for cooling the products: 6a
- a reactor for the final conversion of CO into CO₂: 11
- a hydrogen-permeable membrane at 60 bar/20 bar : 7
- a hydrogen compression element: 8
- an H₂ storage reservoir: 10
- 25 - a carbon dioxide condenser at 60 bar: 14
- a water condenser at 60 bar: 13
- a second cooling exchanger at 60 bar: 6b
- a post-combustion of the final products at 60 bar: 12
- a storage container for the CO₂ at 60 bar: 16
- 30 - a water reservoir at 60 bar: 15

The production unit 1 is used to produce pure hydrogen. The latter is stored under high pressure (200 to 350 bar or more) for later use. The pressure in the conversion reactors 4 of this unit is on the order of 50 to 60 bar. Downstream from the membrane 7, the pressure of the flow of hydrogen extracted is still significant (20 to 30 bar); the compression effort required to reach the storage pressure is thus considerably reduced.

We will now describe Fig. 4, which illustrates, in block diagram form, another variant of embodiment of a unit for producing pure hydrogen, intended to be used immediately in a low-temperature, low-pressure PEMFC-type fuel cell.

The production unit, also called the device 1, is composed of the following elements:

- 10 - a hydrocarbon reservoir: 2
- a reservoir for oxygen under pressure or in liquid form: 3
- a CO + H₂ conversion reactor at 60 bar: 4
- a means for preheating the reagents: 5
- a heat exchanger for cooling the products: 6
- 15 - a reactor for the final conversion of CO into CO₂: 11
- a hydrogen-permeable membrane at 60 bar/20 bar : 7
- a carbon dioxide condenser at 60 bar: 14
- a water condenser at 60 bar: 13
- a cooling exchanger at 60 bar: 6
- 20 - a post-combustion of the final products at 60 bar: 12
- a storage container for the CO₂ at 60 bar: 16
- a water reservoir at 60 bar: 15
- an air compression element at 1 bar/2 bar: 19
- an element for reducing the pressure of the hydrogen from 20 bar/2 bar: 18
- 25 - a PEFC fuel cell at 2 bar and 80°C: 17

The production unit 1 produces pure hydrogen, which is immediately put to use in another system, for example a PEMFC (Proton Exchange Membrane Fuel Cell) type fuel cell 17, running at a relatively low temperature (60 to 120°C) and low pressure (between 1 and 5 bar). The production unit is identical to the one in Fig. 3 until just downstream from the membrane 7, where the pressure of the flow of hydrogen extracted is still significant (20 to 30 bar) and its temperature is high (350°C). The release of pressure from the hydrogen

downstream from the membrane 7 by means of a turbo compressor 18, 19 supplies the energy for compressing the air that feeds the cell 17, which normally requires a piece of auxiliary equipment that is costly in terms of the overall efficiency of the method.

We will now describe Fig. 5, which represents, in block diagram form, another variant of embodiment of a unit for producing a mixture of hydrogen and carbon dioxide, intended to be used immediately in a low-temperature, medium-pressure PEMFC-type fuel cell. The production unit, also called the device 2, is composed of the following elements:

- a hydrocarbon reservoir: 2
- a reservoir for oxygen under pressure or in liquid form: 3
- 10 - a CO + H₂ conversion reactor at 60 bar: 4
- a means for preheating the reagents: 5
- a first heat exchanger for cooling the products: 6a
- a reactor for the final conversion of CO into CO₂: 11
- a water condenser at 7 bar: 13
- 15 - a second heat exchanger for cooling the products: 6b
- a post-combustion of the final products at 7 bar: 12
- a water reservoir at 7 bar: 16
- an air compression element at 1 bar/7 bar: 19
- an element for reducing the pressure of H₂/CO₂ from 60 bar/7 bar: 18
- 20 - a CO₂ storage container at 7 bar: 15

The production unit 1 produces hydrogen for immediate use in a mixture with CO₂ in a fuel cell 17 at a relatively low temperature and medium pressure. In the case of this variant of embodiment, the production unit 1 does not include a hydrogen permeation membrane 7, but includes an additional cooling 6b of the products during the final conversion of the CO into CO₂. The hydrogen production unit 1 operates at a high level of pressure (30 to 60 bar). The energy recovered during the release of pressure 18, 19 from the H₂/CO₂ mixture makes it possible to compress the air admitted into the fuel cell 17. The recoverable energy is substantial since the mass and volume rate of the H₂+CO₂ mixture whose pressure is to be reduced is higher than in the case of the production unit represented in Fig. 4. It is possible to have the cell 17 run at a higher pressure (5 or 7 absolute bar rather than 1 bar), which

promotes the recycling of the water leaving the cell 17 in order to feed the conversion reactor 4, and which also promotes the compactness of the equipment.

We will now describe Fig. 6, which illustrates, in block diagram form, another variant of embodiment of a unit for producing a mixture of hydrogen and carbon dioxide, intended to be used immediately in a high-temperature, medium-pressure SOFC-type fuel cell.

The production unit, also called the device 1, is composed of the following elements:

- a hydrocarbon reservoir: 2
- a reservoir for oxygen under pressure or in liquid form: 3
- a CO + H₂ conversion reactor at 60 bar: 4
- a means for preheating the reagents: 5
- a first heat exchanger for cooling the products: 6a
- a water condenser at 7 bar: 13
- a second cooling exchanger at 7 bar: 6b
- a post-combustion of the final products, CO/H₂ at 7 bar: 12
- a water reservoir at 7 bar: 15
- an air compression element at 1 bar/7 bar: 19
- an element for reducing the pressure of H₂/CO₂ from 60 bar/7 bar: 18
- an SOFC fuel cell at 7 bar and 800°C: 20
- a CO₂ storage container at 7 bar: 16

The production unit 1 produces hydrogen in a mixture with CO and CO₂ for use in an SOFC (Solid Oxide Fuel Cell) type fuel cell running at a high temperature (600 to 900°C) and relatively medium pressure (between 1 and 7 bar). In the case of this other variant of embodiment, the production unit 1 does not include a hydrogen-permeable membrane 8 either; nor does it include the final conversion 11 of the CO into CO₂ since the CO can be used by the SOFC. The hydrogen production unit 1 operates at a high level of pressure (30 to 60 bar). The energy recovered during the release of pressure 18 from the H₂/CO/CO₂ mixture makes it possible to compress the air 19 admitted into the fuel cell 17. It is possible to have the SOFC run at a medium pressure (5 or 7 absolute bar instead of 1), which promotes the recycling of the water leaving the cell in order to feed the conversion reactor 4, as well as the compactness of the equipment.

The means for preheating the reagents 5 and the heat exchanger for cooling 6 the products in the case of the variants of embodiment illustrated in Figs. 3 through 6 may advantageously be combined so that the energy recovered from the products is transferred to the reagents. Both capabilities of the combination, regeneration or recovery, can be
5 implemented in the variants of embodiment described above.

We will now describe Fig. 7, which illustrates a variant of embodiment of a means for preheating the reagents 5 and a heat exchanger for cooling the associated products 6, constituting a regenerative system. In the case of the variant of embodiment represented in Fig. 7, the reagent preheating means previously referenced 5 is referenced 22, and the
10 cooling heat exchanger previously referenced 6 is referenced 23.

In the case of regenerative exchangers, the heat is stored in the elements made of ceramic material placed in the reagent preheating means 22 and in the cooling heat exchanger 23. The reagent preheating means 22 and the cooling heat exchanger 23 are disposed on either side of the conversion reactor 4.

15 The flows are periodically alternated. The cold reagents enter the reagent preheating means 22, wherein the ceramic elements are hot, heat up on contact with it and cool it, while the hot products enter the cooling heat exchanger 23, which is relatively cold, cool off in contact with the ceramic elements and reheat them. After a certain amount of time (on the order of one minute to 30 minutes depending on the size of the installation), the flows are
20 reversed by means of valves 21, and the roles of the reagent preheating means 22 and the cooling heat exchanger 23 are reversed. The reagents flow into the cooling heat exchanger 23, which has become hot enough to serve as the reagent preheating means 22, then pass through the conversion reactor 4 in the opposite direction. The conversion products leave the conversion reactor 4 in the direction of the reagent preheating means 22. The latter has
25 become cold enough to serve as the cooling heat exchanger.

The ceramic elements have the advantage of being able to be used at a very high temperature.

We will now describe Fig. 8, which represents a variant of embodiment of a means for preheating the reagents 5 and a heat exchanger for cooling the associated products 6, constituting a recovery system 24.
30

In the case of the variant of embodiment represented in Fig. 8, the means for preheating the reagents 5 and the heat exchanger for cooling the products 6 form two sides of the same piece of equipment, and the heat is transferred from one to the other through the impermeable surface that separates them. This configuration has the advantage of continuous operation and does not require a system of flow-reversing and control valves. The thermal inertia is also much lower.

The hydrocarbons, the oxygen and the water or vapor enter the recovery system 24, where they are heated, cooling the hot products of the conversion. They are then injected into the conversion reactor 4 on the opposite side of the recovery system 24 through feed circuits 25. The hot conversion products then enter the recovery system 24.

In the case of the four variants of embodiment represented in reference to Figs. 3 through 6, after the extraction of the hydrogen or its use by the fuel cell, the gas may still contain a small amount of residual hydrogen. The same is true of the CO after its conversion into CO₂ or its use by the SOFC-type fuel cell. The gas is then subjected to a post-combustion 12 of these residues, which transforms them into H₂O and CO₂.

The gas, under high pressure (50 or 60 bar in the case of the variants of embodiment in Figs. 3 and 4) or medium pressure (5 to 7 bar in the case of the variants of embodiment in Figs. 5 and 6), no longer contains anything other than water vapor and carbon dioxide (with small traces of CO, H₂ if the post-combustion is incomplete, and nitrogen if the oxygen used is not pure). Cooling it to a temperature on the order of 40°C will result in the condensation 13 of nearly all of the water, which can be recycled back to the beginning of the hydrocarbon conversion process via a reservoir of water under pressure 15.

The residual gas is then nothing but nearly pure CO₂ (with traces of CO, H₂, N₂, H₂O). At a pressure of 60 bar, the CO₂ can be easily condensed by cooling in contact with a wall at ambient temperature. The effective rate of condensation of the CO₂ will depend on the temperature of the cold wall and the level of residual impurities in the gas: for example, at 60 bar and with a wall at 10°C, a 92% to 99.2% condensation of the CO₂ will be obtained if the traces of CO, H₂ and N₂ represent 2% to 0.2%, respectively, in the products leaving the post-combustion chamber. The CO₂ can then be stored in dense liquid form. Pressures as low as 30 bar are acceptable for condensing the CO₂; in that case, it is necessary to use a

refrigerant at negative temperatures such as -20°C in order to obtain substantial levels of CO₂ condensation, commensurate with the level of residual impurities in the gas.

In the case of the variants represented in Figs. 5 and 6, the flow of CO₂ generated can be stored at a pressure of 7 bar, or possibly recompressed in order to be condensed.

5 In all cases, it is possible not to discharge the CO₂ generated by the hydrocarbon conversion into the atmosphere. It may be re-used in a CO₂-consuming process or stored in underground layers. Finally, if the hydrogen is from a fossil hydrocarbon source, its production will not have generated any additional greenhouse effect. If the hydrogen is from a renewable biomass source, its production is accompanied by a carbon sink.

10 Figs. 3 and 4 show two variants of embodiment comprising two successive steps. The purpose of one step is to convert CO in to CO₂ using the gas's catalytic reaction to water: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$. The purpose of the other step is to extract the hydrogen formed by means of a membrane 7. The use of oxygen in place of air promotes the extraction by the membrane 7 since the partial pressure of the hydrogen, which is not diluted in nitrogen, is
15 higher.

Moreover, it is advantageous to be able to combine several functions in the same piece of equipment. The use of a vector gas or an easily condensable extraction gas, for example water vapor or ammonia, downstream from the permeation membrane 7, makes it possible to lower the partial pressure of the hydrogen downstream and thus to extract more of
20 the hydrogen in the reformat. Fig. 9 shows the increase in the efficiency of the hydrogen extraction as a function of the ratio between the molar flow rate of the hydrogen to be extracted and the molar flow rate of the flow of extraction gas. In the case illustrated in Fig. 9, the total pressure upstream from the membrane 7 is 45 bar, the molar fraction of the hydrogen upstream is 50.9%, and the total pressure downstream from the membrane 7 is 5
25 bar. Extraction efficiencies of 90 to 100% may be obtained, even with back pressures of 5 bar downstream from the membrane 7. After the extraction of the hydrogen, the flow of extraction gas may be condensed by cooling so as to be recycled to the extraction membrane, leaving behind a flow of pure hydrogen to be used or stored.

Any gas that is inert with respect to hydrogen and the membrane, such as nitrogen, argon, water vapor, ammonia, etc., may be used to lower the partial pressure of the hydrogen
30 downstream from the membrane and thus extract the hydrogen more easily. However, it is

advantageous to use an easily condensable extraction gas such as water vapor or ammonia; a step for cooling and condensing the vector gas/hydrogen mixture will make it possible to separate them and to recover pure hydrogen.

We will now describe, in reference to Figs. 10a and 10b, two variants of embodiment according to the invention of a reactor for the final conversion of CO into CO₂ 11, comprising a hydrogen-permeable membrane 7 that makes it possible to extract the hydrogen. In the case of low-capacity, small scale installations, it is possible to organize the permeation chamber 27 so that it is concentric to the conversion reactor. In the case of the variant of embodiment represented in Fig. 10a, the hydrogen is extracted at the center of the final conversion reactor 11.

The membrane tube 26 is placed on the axis of the chamber 27 and is fed with extraction water vapor. The conversion catalyst is placed in the ring-shaped chamber around the membrane tube 26 and is passed through by the gasses to be converted, generally in the opposite direction from the extraction water vapor.

In the case of the variant of embodiment represented in Fig. 10b, the hydrogen is extracted at the periphery of the final conversion reactor 11. The water vapor for extracting the hydrogen circulates at the periphery of the final conversion reactor 11. The conversion catalyst is placed in the center.

We will now describe, in reference to Fig. 11, another variant of embodiment according to the invention of a reactor for the final conversion of CO into CO₂ 11, equipped with a series of closed-end tubes that descend into the core of the reactor, each of which supports a hydrogen-permeable membrane that makes it possible to extract hydrogen.

In the case of a high-capacity installation, the membrane surface to be installed would result in an excessive diameter and length if the configuration represented in Fig. 10a or 10b were retained. Likewise, the quantity of catalyst required would result in a ring that is too thick. For this reason, the compositions and temperatures in each section would not be homogeneous. It is preferable to divide up the catalyst thickness using a number of membrane tubes 26 shaped like the fingers of a glove. The tubes 26, of small diameter and length, descend from the external wall right into the core of the conversion reactor 11.

Reactors like those described in reference to Figs. 10a and 10b make it possible not to separate the steps for the final CO/CO₂ conversion and for the extraction of the hydrogen.

They are performed in the same chamber. It is thus possible to reduce the partial pressure of the hydrogen during the final CO/CO₂ conversion and thereby shift the equilibrium toward the formation of CO₂ and H₂O; the conversion reaction is accelerated. A smaller quantity of catalyst or a smaller size chamber may be used to achieve equivalent performance. This configuration is possible because the conversion of the CO into CO₂ and the extraction through a hydrogen-permeable membrane are done at the same temperature level: on the order of 250 to 400°C. The reaction of the gas to water is exothermic, and heat must be extracted in order to maintain the gas within the optimal operating temperature range of the catalyst. In the case where the membrane is located inside the final conversion reactor, the flow of extraction water vapor can advantageously be used to cool the CO/CO₂ conversion chamber. Likewise, when the installation is cold and must be reheated in order for the catalyst and the permeable membrane to reach their best operating temperature range, the flow of extraction water vapor may be used to supply heat to this conversion reactor. The tube or tubes that support the permeation membrane 26 and are passed through by the extraction water vapor can advantageously serve as heat exchangers, thus avoiding the use of specific equipment for this heat exchange function. The temperature of the conversion chamber can thus be regulated by varying the flow rate and the temperature of the flow of extraction water vapor.

Nitrogen may be produced by distilling air under cryogenic conditions. The production of one kg of nitrogen is accompanied by the production of 0.30 kg of oxygen. This oxygen, in liquid form, may be used onsite to produce hydrogen using the method according to the invention described in reference to Figs. 3 through 6. It may also be transported in order to be used at another site using the method according to the invention described in reference to Figs. 3 through 6.

With the oxygen produced, for an 80 to 90% energy efficiency of the method for producing hydrogen, the consumption of diesel fuel is respectively equal to 0.21 kg/kg of nitrogen and 0.26 kg/kg of nitrogen for a quantity of captured CO₂ respectively equal to 0.67 kg per kg of nitrogen and 0.82 kg per kg of nitrogen. The quantity of hydrogen generated is respectively equal to 0.054 kg of H₂ per kg of nitrogen produced and 0.073 kg of H₂ per kg of nitrogen produced, representing a chemical energy of 7.7 to 10 MJ and an electrical energy of 1.1 to 1.45 kWh after use in a fuel cell.

Hydrogen can also be produced by water electrolysis. The production of one kg of electrolytic hydrogen is accompanied by the production of 8 kg of oxygen. The electrolyzers operate under medium pressure, from a few bar to several tens of bar. The oxygen produced may be put to use according to any of the variants of embodiment represented in Figs. 3 through 6. The variant of embodiment represented in Fig. 3, however, has the advantage of using the oxygen onsite to produce hydrogen. The method according to the invention makes it possible to obtain a flow of chemical hydrogen in addition to the electrolytic hydrogen, while contributing to CO₂ capture and to the amortization of all the utilities for conditioning the hydrogen produced.

10 The leverage is considerable, since with 8 kg of oxygen produced, for an 80 to 90% energy efficiency of the chemical method for producing hydrogen, the consumption of diesel fuel is respectively equal to 5.75 to 6.9 kg/kg of electrolytic hydrogen for a quantity of captured CO₂ respectively equal to 19.1 kg per kg of electrolytic hydrogen and 21.8 kg per kg of electrolytic hydrogen. The quantity of hydrogen generated is respectively equal to 1.45
15 kg of chemical hydrogen per kg of electrolytic hydrogen and 1.96 kg of chemical hydrogen per kg of electrolytic hydrogen.

Combining the two methods results in an increase in the quantity of hydrogen produced by a factor of nearly 3, which largely compensates for the efficiency loss of electrolysis.